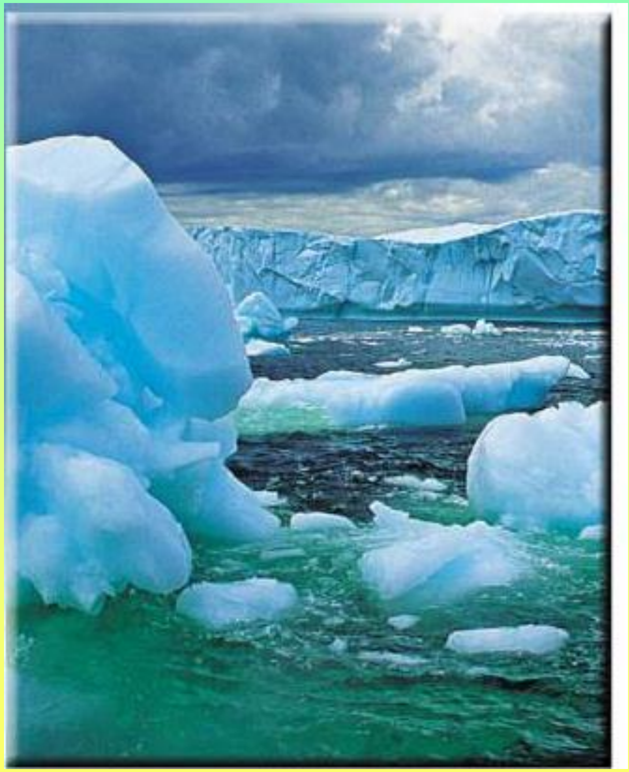


Intermolecular Forces
and
Liquids and Solids

A ***phase*** is a homogeneous part of the system in contact with other parts of the system but separated from them by a well-defined boundary.

<u>2 Phases</u>

Solid phase - ice

Liquid phase - water

TABLE 11.1

Characteristic Properties of Gases, Liquids, and Solids

State of Matter	Volume/Shape	Density	Compressibility	Motion of Molecules
Gas	Assumes the volume and shape of its container	Low	Very compressible	Very free motion
Liquid	Has a definite volume but assumes the shape of its container	High	Only slightly compressible	Slide past one another freely
Solid	Has a definite volume and shape	High	Virtually incompressible	Vibrate about fixed positions

Intermolecular Forces

Intermolecular forces are attractive forces **between** molecules.

Intramolecular forces hold atoms together in a molecule.

Intermolecular vs Intramolecular

- 41 kJ to vaporize 1 mole of water (**inter**)
- 930 kJ to break all O-H bonds in 1 mole of water (**intra**)

Generally, **inter**molecular forces are much weaker than **intra**molecular forces.

"Measure" of intermolecular force

boiling point

melting point

ΔH_{vap}

ΔH_{fus}

ΔH_{sub}

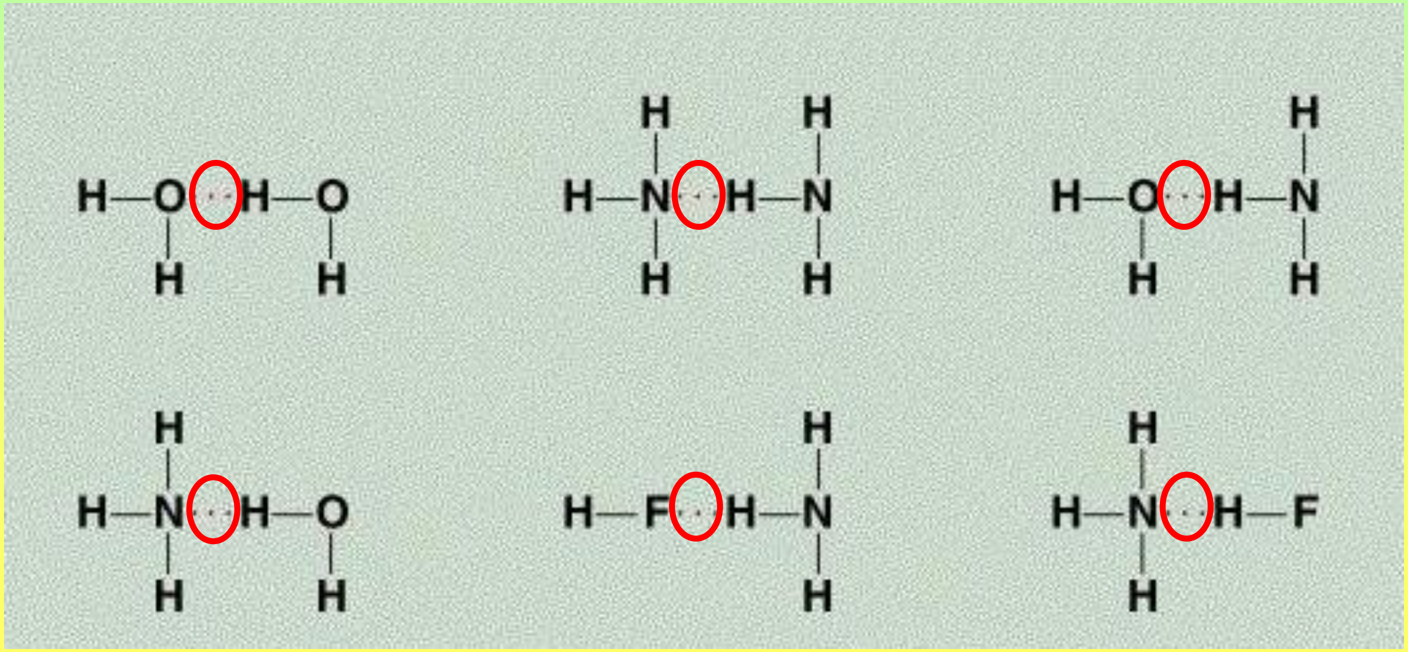
Types of Intermolecular Forces

1. Hydrogen Bond (strongest)

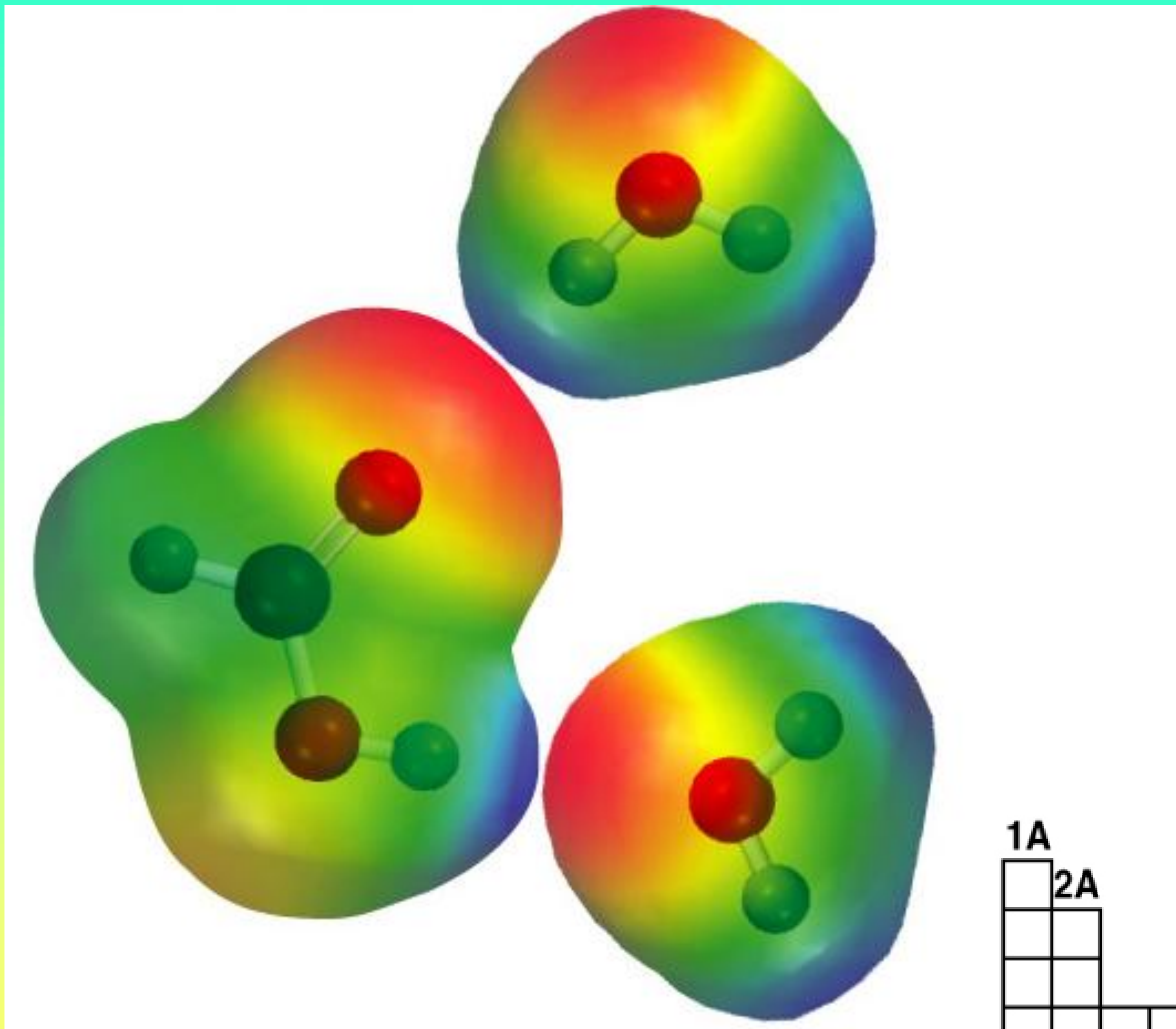
The ***hydrogen bond*** is a special dipole-dipole interaction between the hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom. IT IS NOT A BOND.

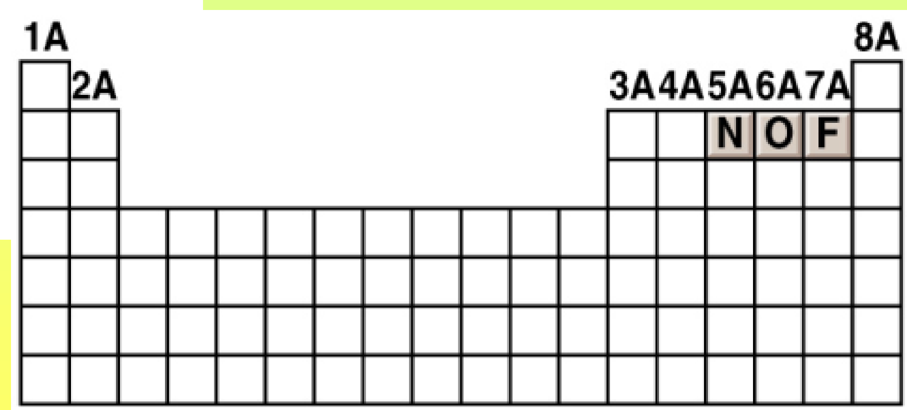
A — H···B or A — H···A

A & B are N, O, or F

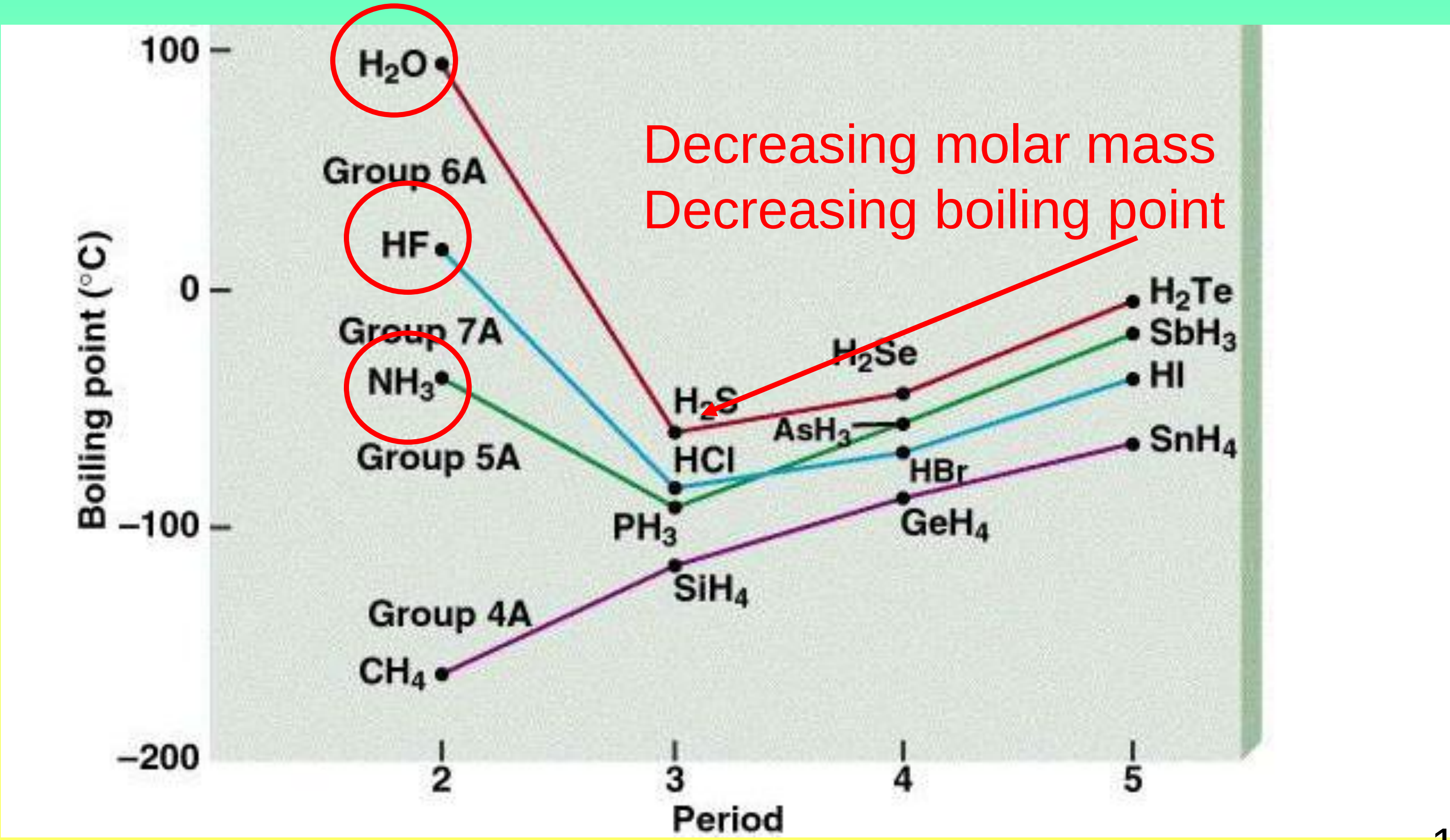


Hydrogen Bond





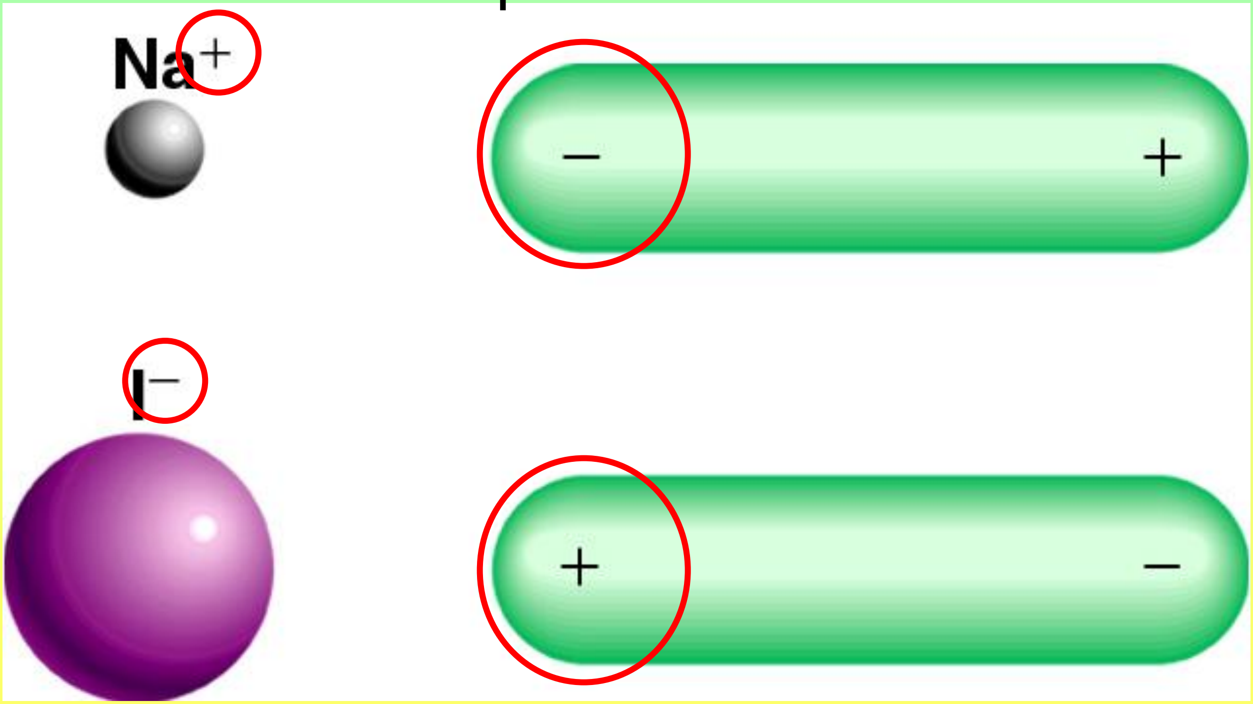
Why is the hydrogen bond considered a "special" dipole-dipole interaction?

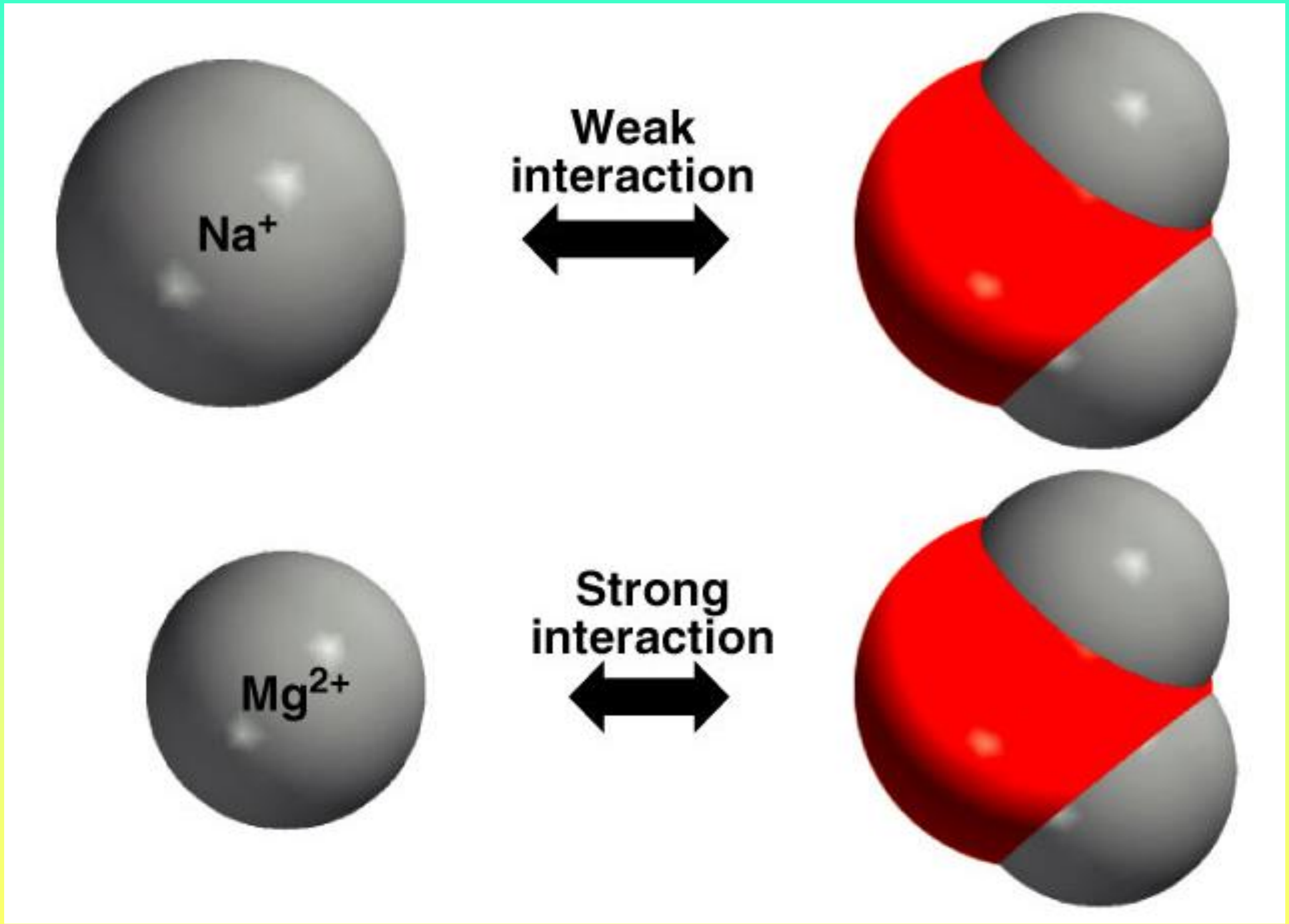


2. Ion-Dipole Forces

Attractive forces between an **ion** and a **polar molecule**

Ion-Dipole Interaction



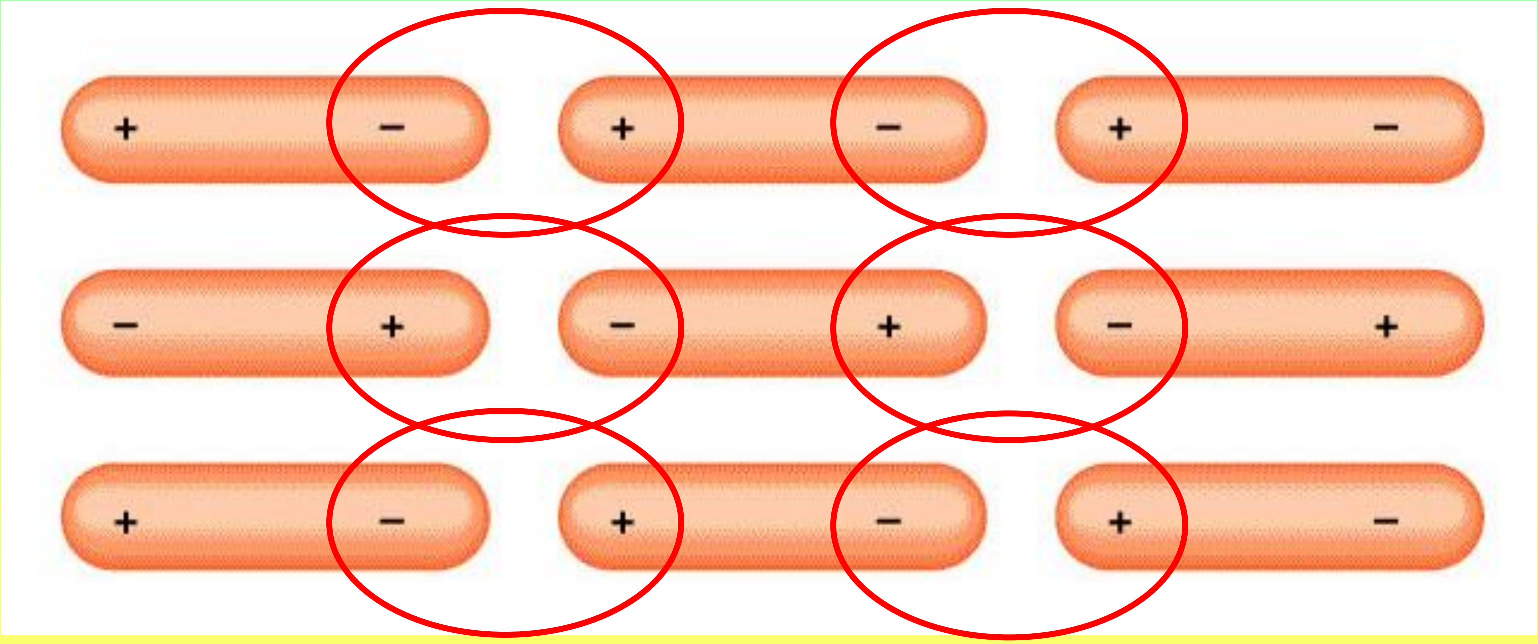

Na+
Weak
interaction
Mg2+
Strong
interaction

Types of Intermolecular Forces

3. Dipole-Dipole Forces

Attractive forces between **polar molecules**

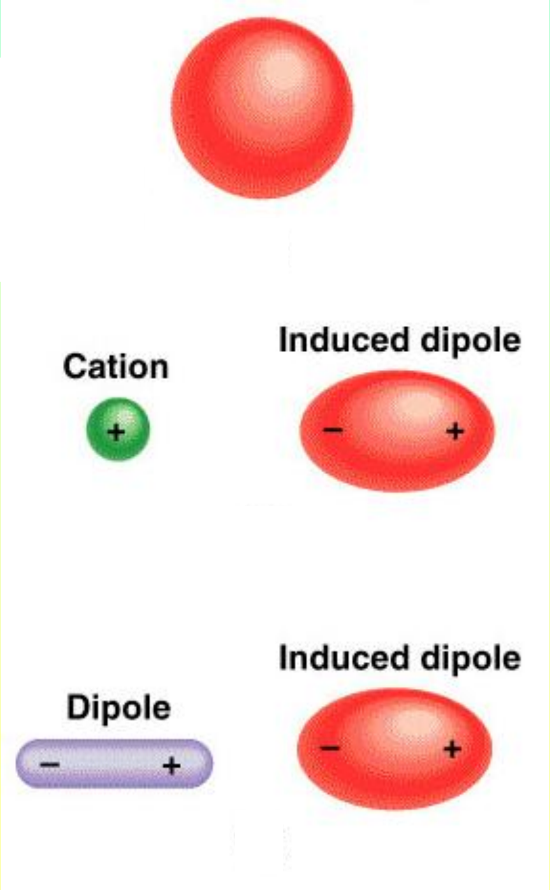
Orientation of Polar Molecules in a Solid



Types of Intermolecular Forces

4. Dispersion Forces – van der Walls forces/London forces (weakest)

Attractive forces that arise as a result of **temporary dipoles induced** in atoms or molecules



ion-induced dipole interaction

dipole-induced dipole interaction

Intermolecular Forces

4. Dispersion Forces Continued

Polarizability is the ease with which the electron distribution in the atom or molecule can be distorted.

Polarizability increases with:

- greater number of electrons
- more diffuse electron cloud

Dispersion forces usually increase with molar mass.

TABLE 11.2 Melting Points of Similar Nonpolar Compounds

Compound	Melting Point (°C)
CH_4	−182.5
CF_4	−150.0
CCl_4	−23.0
CBr_4	90.0
CI_4	171.0

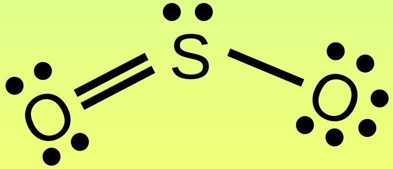
What type(s) of intermolecular forces exist between each of the following molecules?

HBr

HBr is a polar molecule: dipole-dipole forces. There are also dispersion forces between HBr molecules.

CH_4

CH_4 is nonpolar: dispersion forces.



SO_2

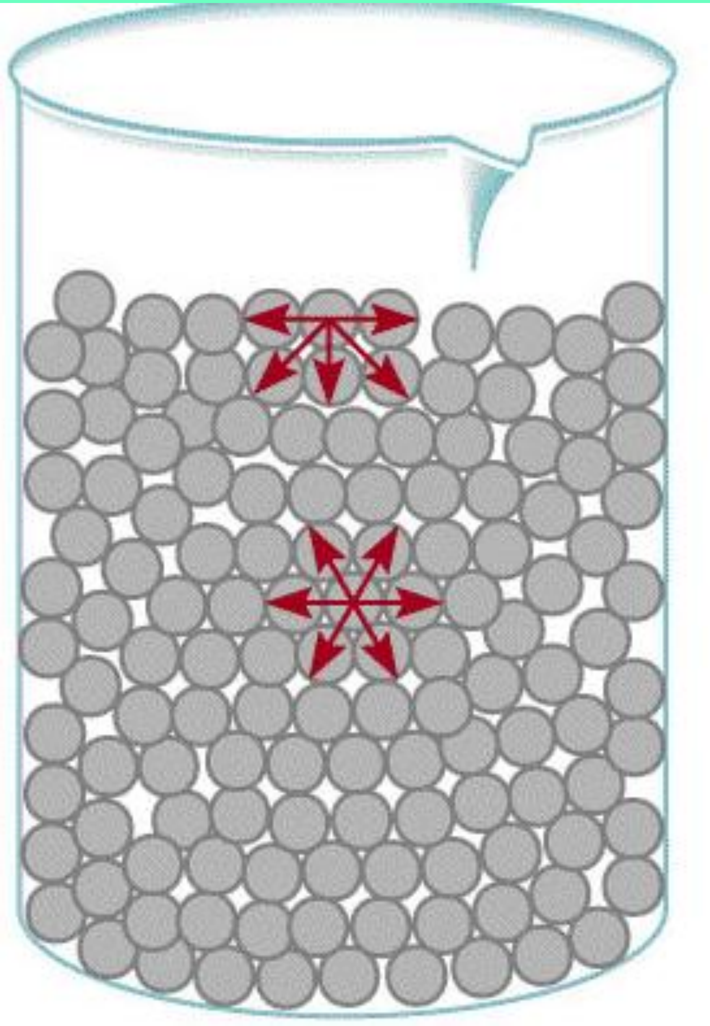
SO_2 is a polar molecule: dipole-dipole forces. There are also dispersion forces between SO_2 molecules.

Properties of Liquids

Surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.

Strong intermolecular forces

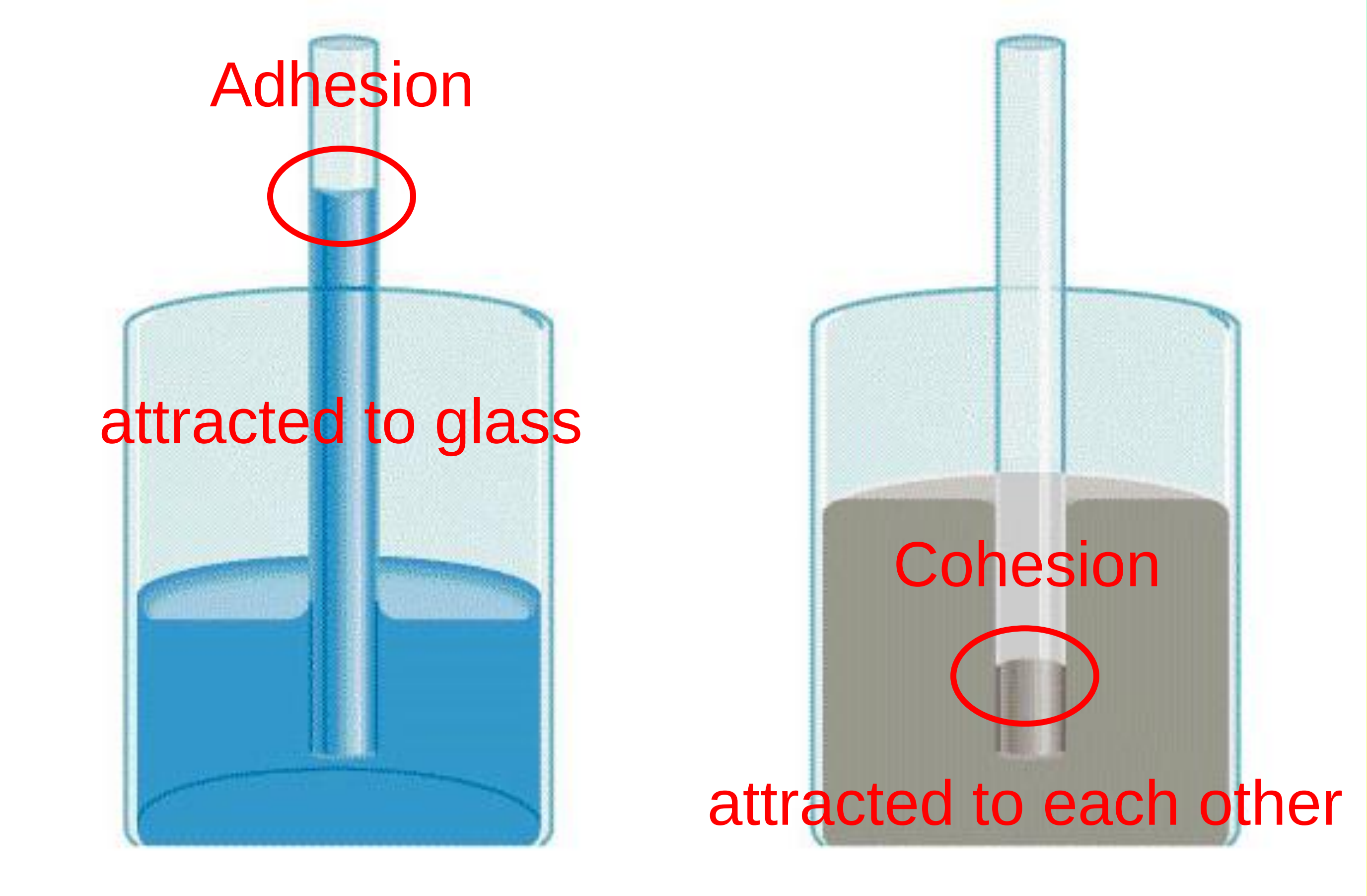
High surface tension



Properties of Liquids

Cohesion is the intermolecular attraction between like molecules

Adhesion is an attraction between unlike molecules



Properties of Liquids

Viscosity is a measure of a fluid's resistance to flow.

Strong intermolecular forces

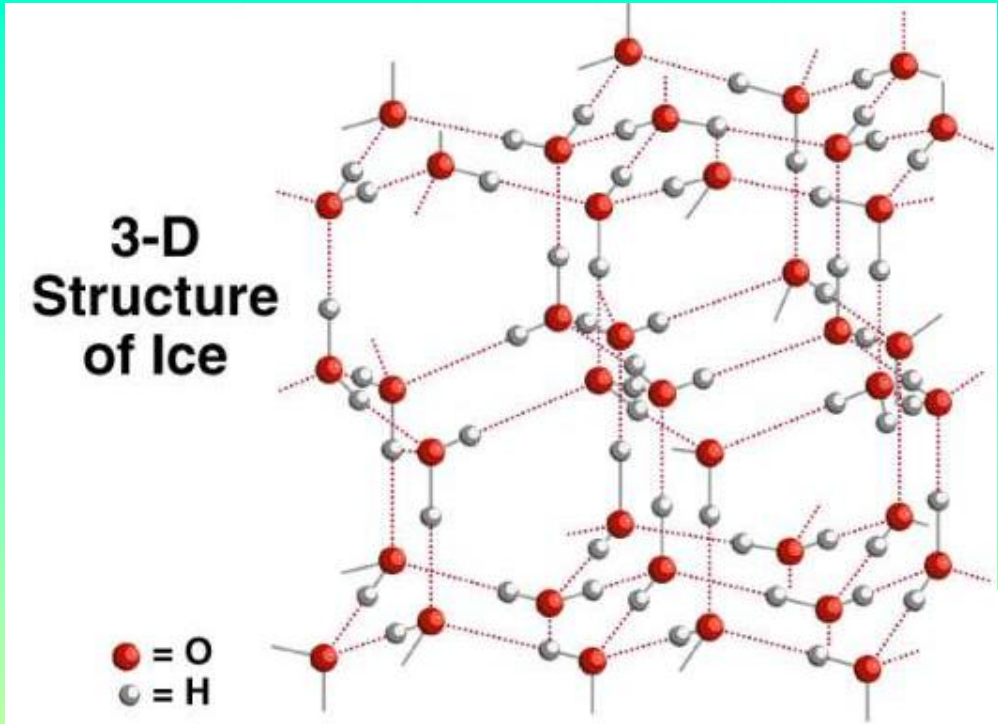
High viscosity

TABLE 11.3

Viscosity of Some Common Liquids at 20°C

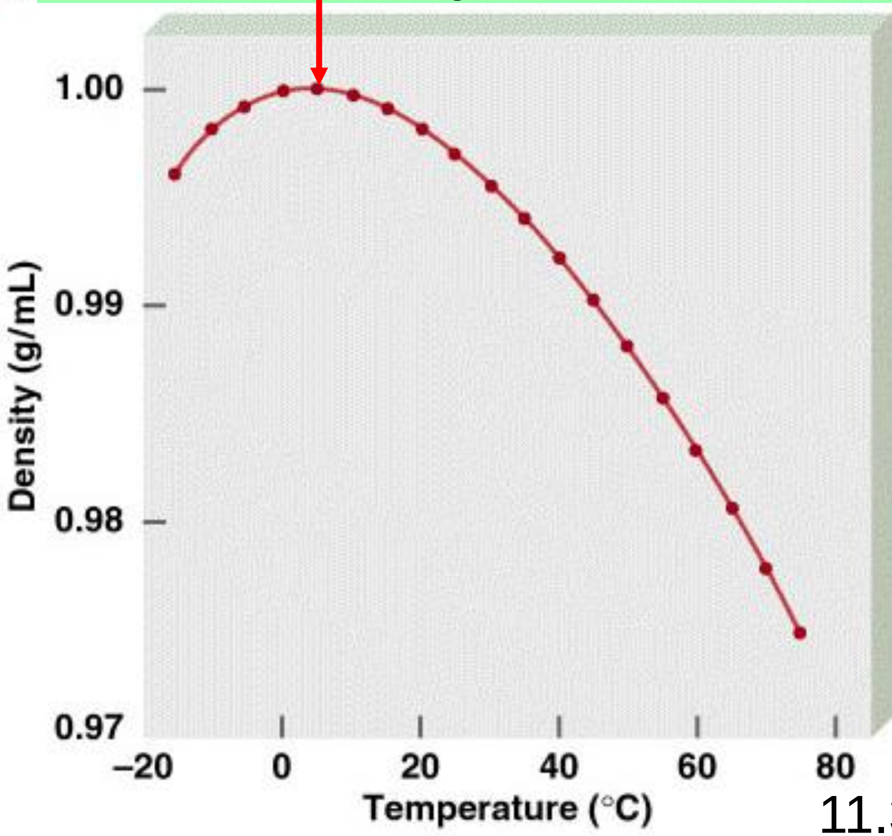
Liquid	Viscosity $(N\ s/m^2)$*
Acetone (C_3H_6O)	3.16×10^{-4}
Benzene (C_6H_6)	6.25×10^{-4}
Blood	4×10^{-3}
Carbon tetrachloride (CCl_4)	9.69×10^{-4}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Diethyl ether ($C_2H_5OC_2H_5$)	2.33×10^{-4}
Glycerol ($C_3H_8O_3$)	1.49
Mercury (Hg)	1.55×10^{-3}
Water (H_2O)	1.01×10^{-3}

Water is a Unique Substance



Maximum Density
4^0C

Density of Water

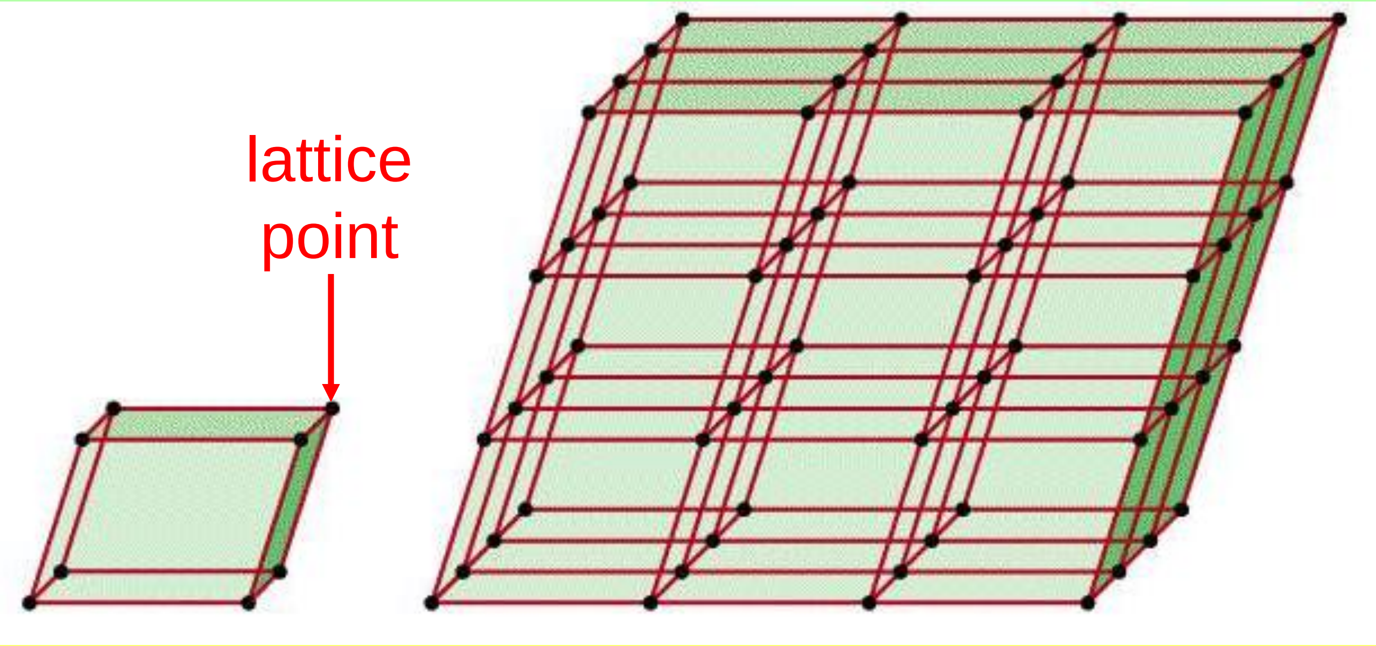


Ice is less dense than water

A ***crystalline solid*** possesses rigid and long-range order. In a crystalline solid, atoms, molecules or ions occupy specific (predictable) positions.

An ***amorphous solid*** does not possess a well-defined arrangement and long-range molecular order.

A ***unit cell*** is the basic repeating structural unit of a crystalline solid.

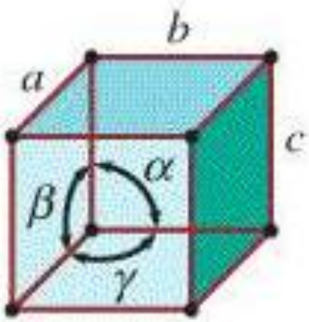


Unit Cell Unit cells in 3 dimensions

At lattice points:

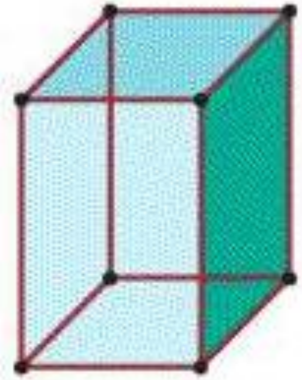
- Atoms
- Molecules
- Ions

Seven Types of Unit Cells

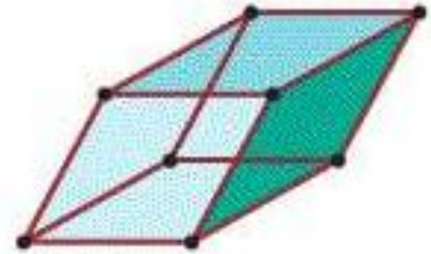


Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$

Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

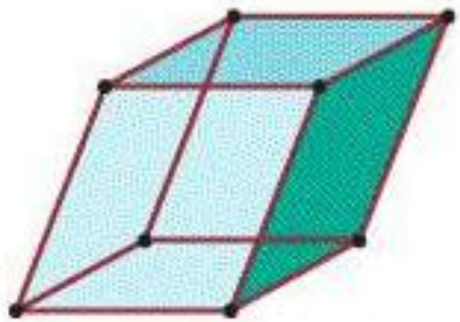


Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

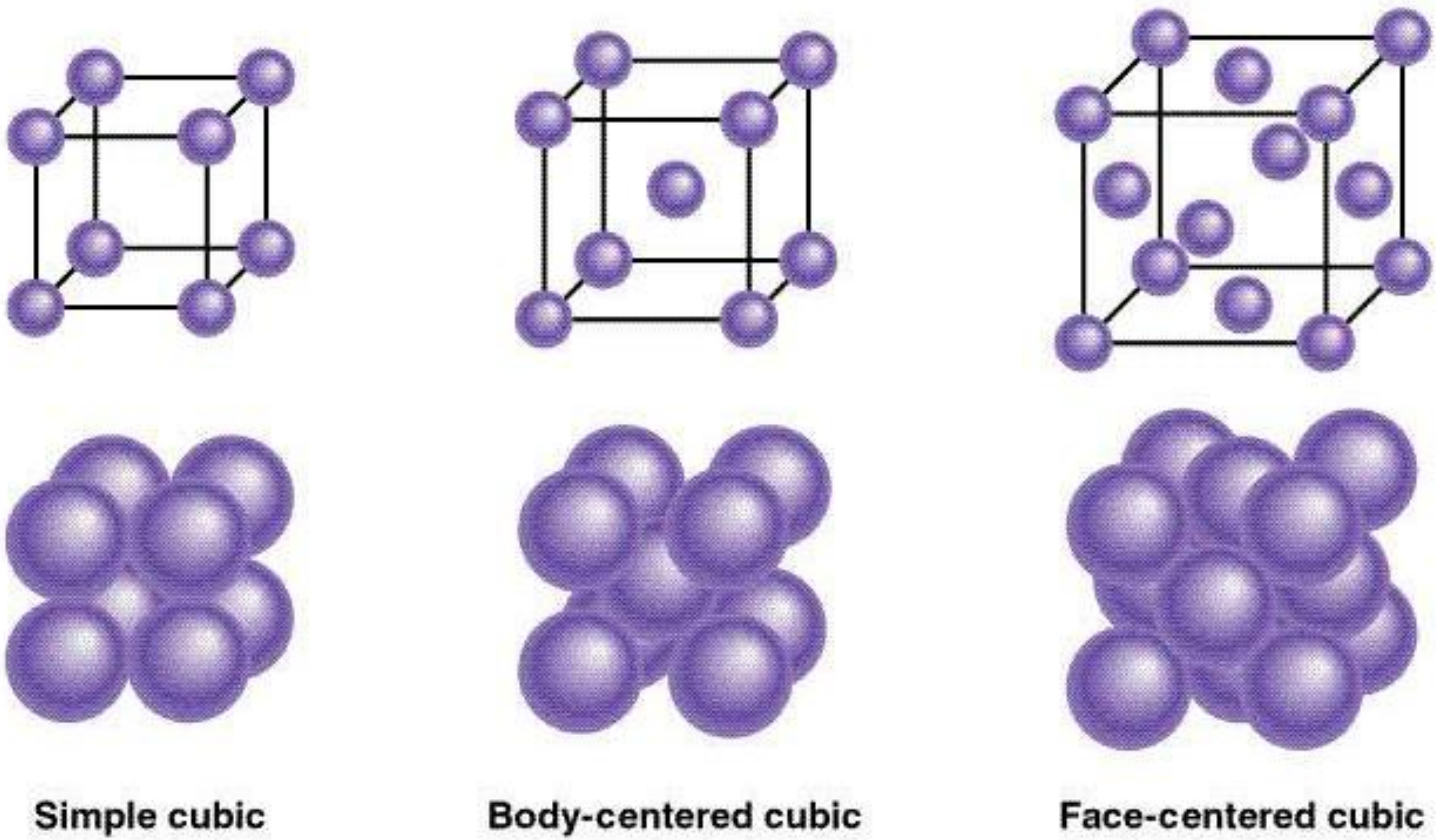
Monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90°, \beta \neq 90°$



Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

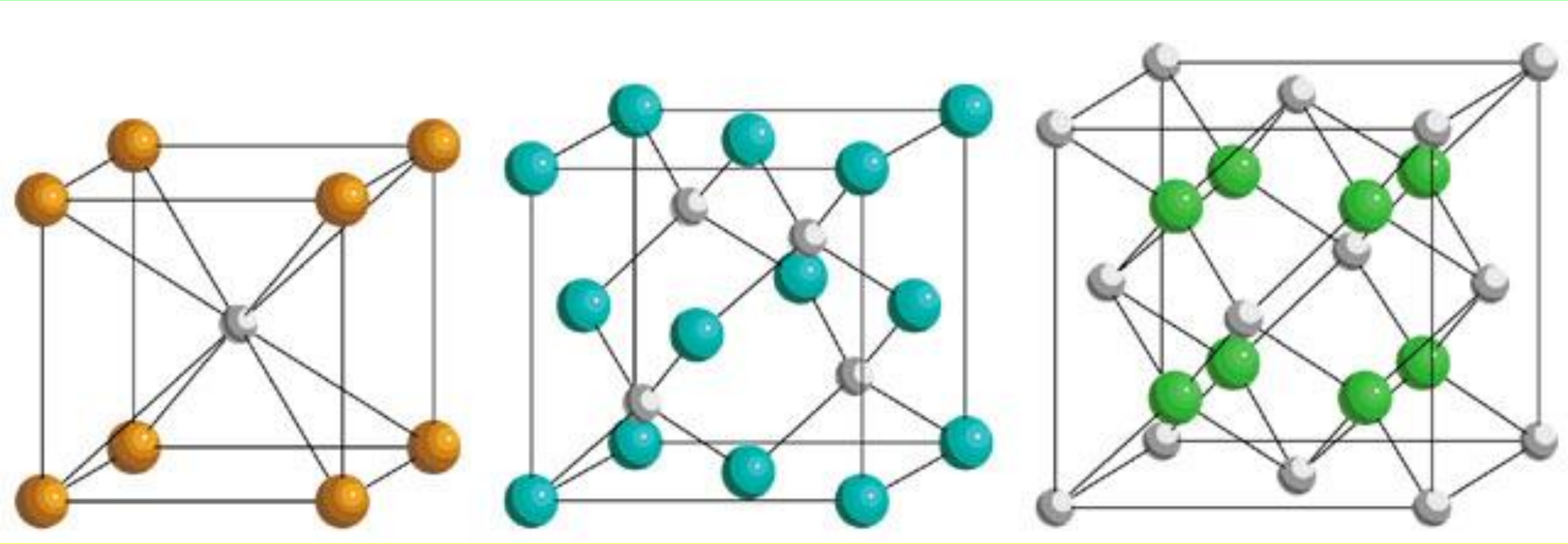
Three Types of Cubic Cells



Types of Crystals

Ionic Crystals – Ion-Ion interactions are the strongest (including the "intermolecular forces" (H bonding, etc.)

- Lattice points occupied by cations and anions
- Held together by electrostatic attraction
- Hard, brittle, high melting point
- Poor conductor of heat and electricity

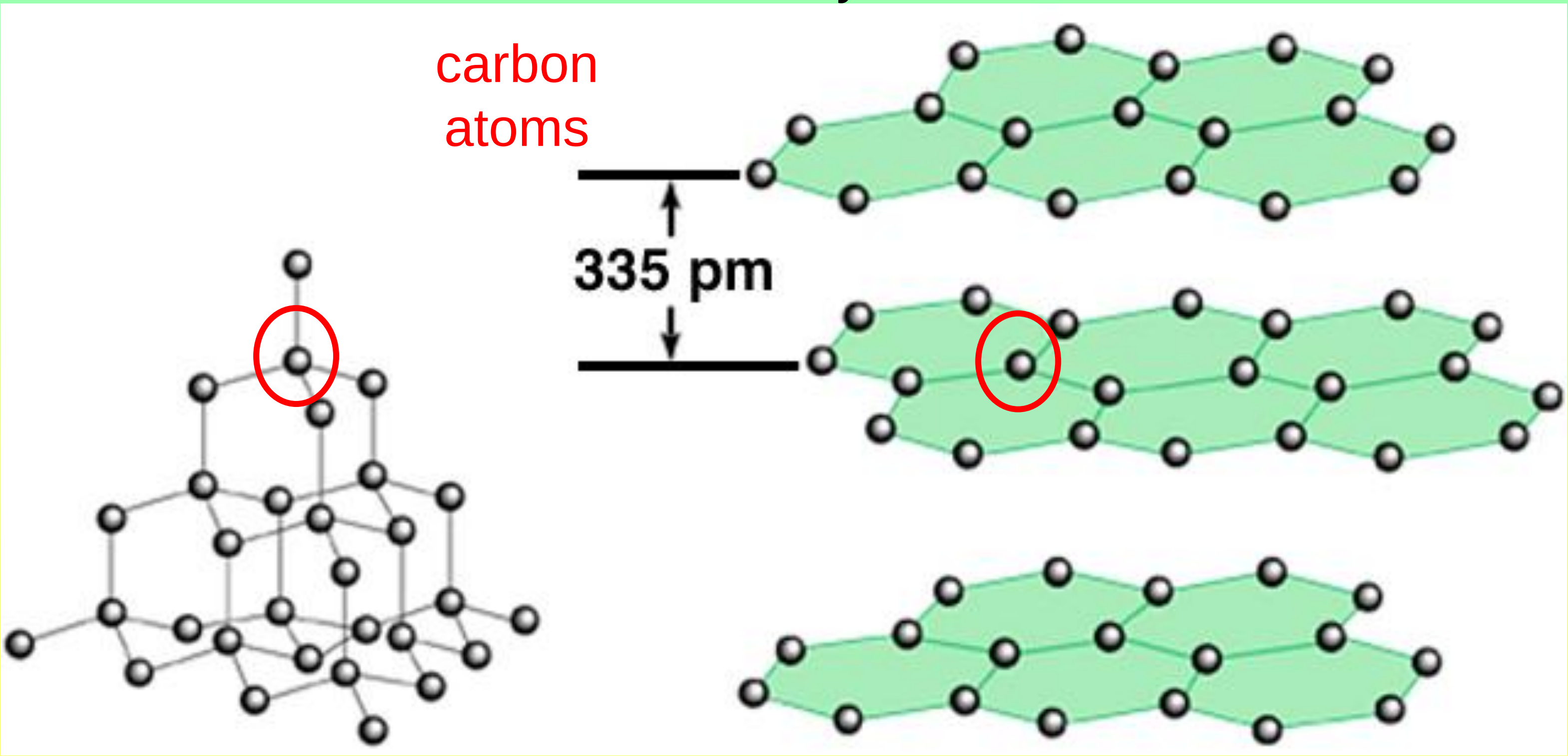


$CsCl$ ZnS CaF_2

Types of Crystals

<u>Covalent Crystals</u> – Stronger than IM forces but generally weaker than ion-ion

- Lattice points occupied by atoms
- Held together by covalent bonds
- Hard, high melting point
- Poor conductor of heat and electricity



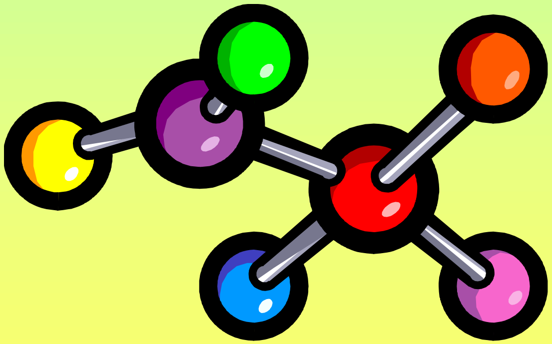
diamond

graphite

Types of Crystals

<u>Molecular Crystals</u>

- Lattice points occupied by molecules
- Held together by intermolecular forces
- Soft, low melting point
- Poor conductor of heat and electricity

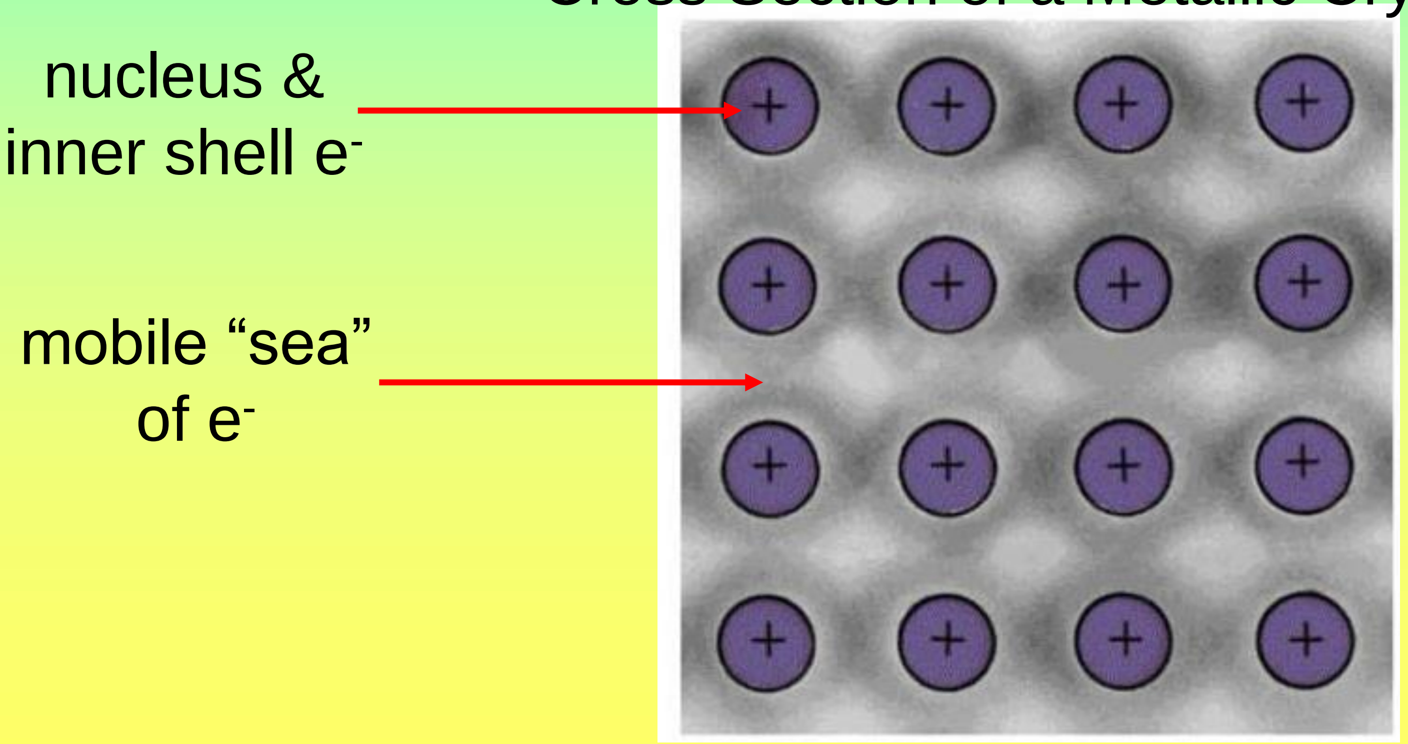


Types of Crystals

<u>Metallic Crystals</u> – Typically weaker than covalent, but can be in the low end of covalent

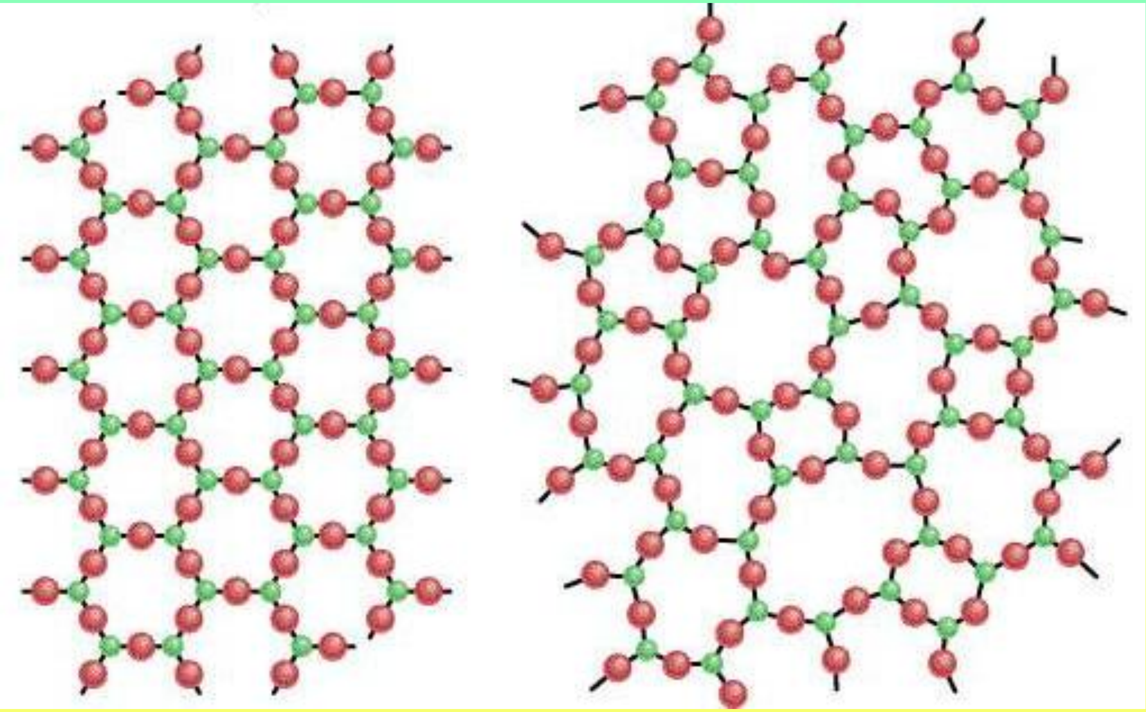
- Lattice points occupied by metal atoms
- Held together by metallic bonds
- Soft to hard, low to high melting point
- Good conductors of heat and electricity

Cross Section of a Metallic Crystal



An ***amorphous solid*** does not possess a well-defined arrangement and long-range molecular order.

A ***glass*** is an optically transparent fusion product of inorganic materials that has cooled to a rigid state **without crystallizing**



Crystalline quartz (SiO_2)

Non-crystalline quartz glass

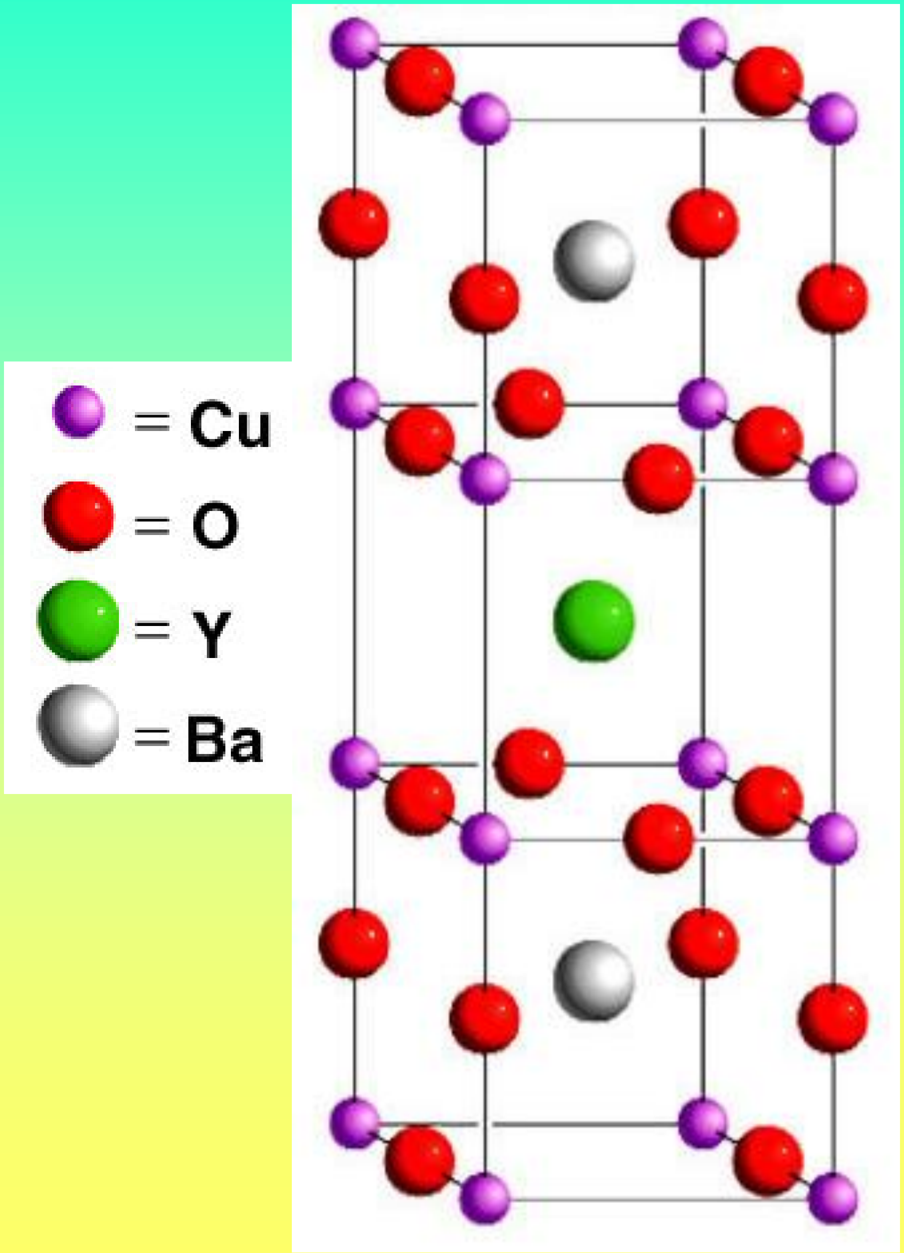
Types of Crystals

TABLE 11.4

Types of Crystals and General Properties

Type of Crystal	Force(s) Holding the Units Together	General Properties	Examples
Ionic	Electrostatic attraction	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, $CaCO_3$
Covalent	Covalent bond	Hard, high melting point, poor conductor of heat and electricity	C (diamond),† SiO_2 (quartz)
Molecular*	Dispersion forces, dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O, $C_{12}H_{22}O_{11}$ (sucrose)
Metallic	Metallic bond	Soft to hard, low to high melting point, good conductor of heat and electricity	All metallic elements; for example, Na, Mg, Fe, Cu

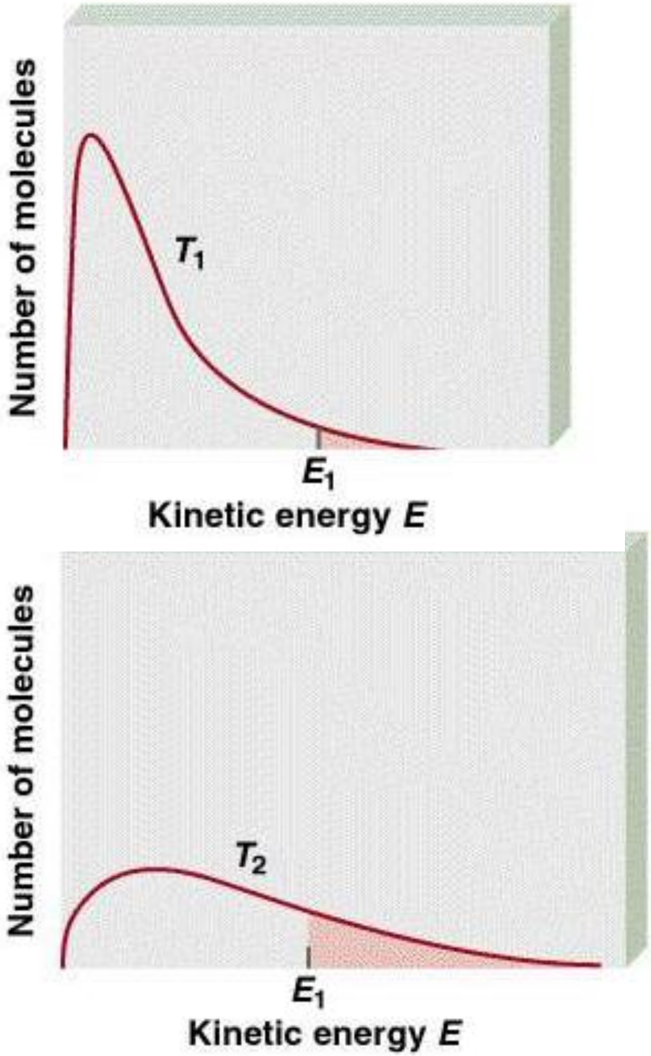
Chemistry In Action: High-Temperature Superconductors



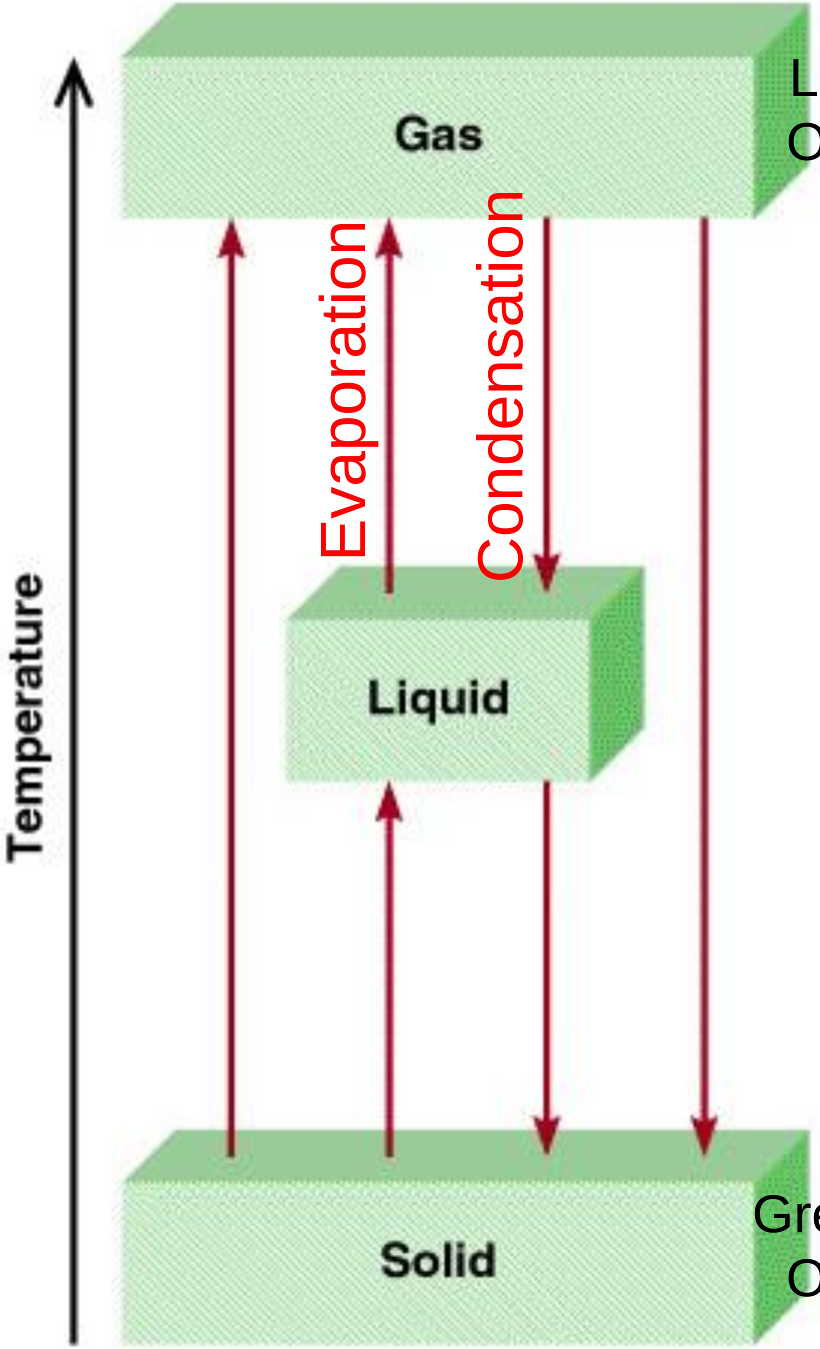
Energetics Teaser

The following is presented as a introduction to the next unit

Phase Changes



$T_2 > T_1$



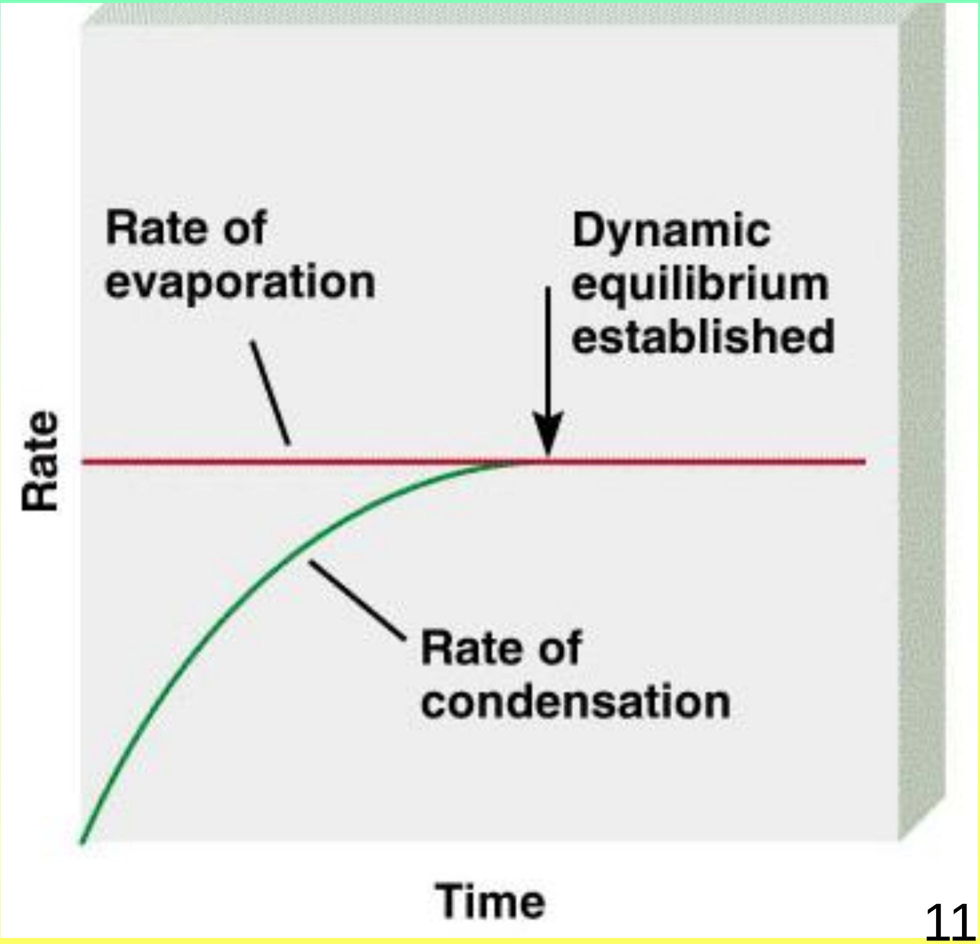
11.8

The ***equilibrium vapor pressure*** is the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

Dynamic Equilibrium

Rate of condensation = Rate of evaporation



Molar heat of vaporization (ΔH_{vap}) is the energy required to vaporize 1 mole of a liquid.

Clausius-Clapeyron Equation

$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$

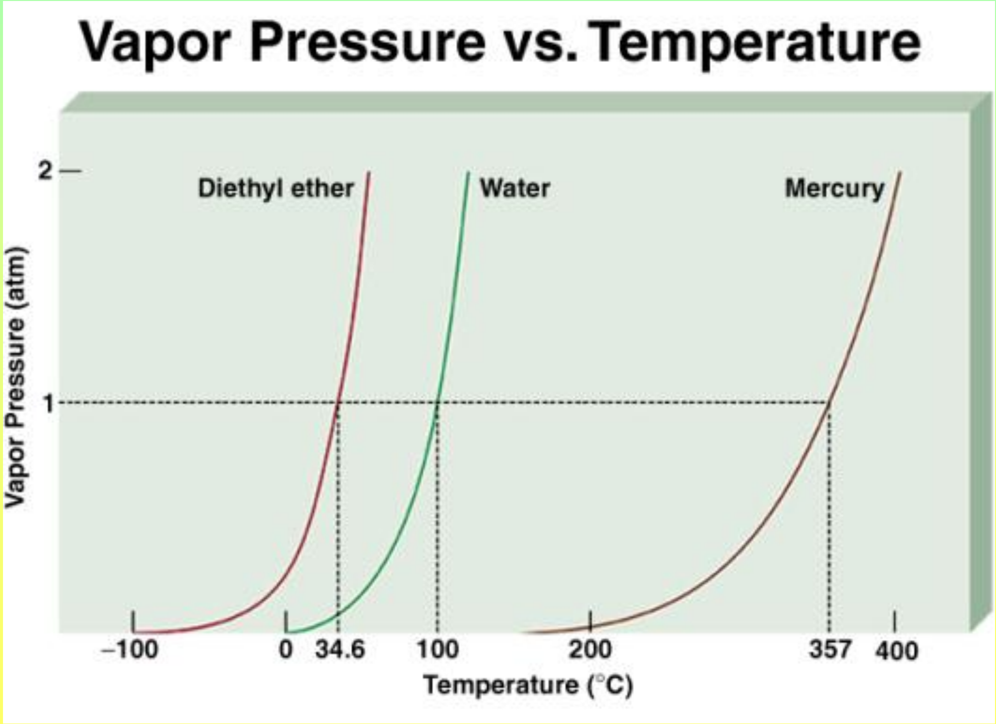
Calculation not on test!

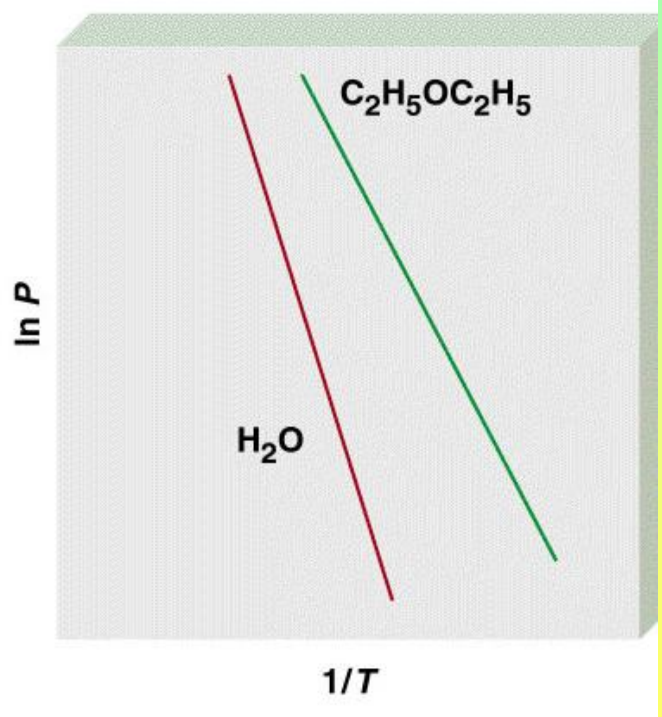
C = constant (depends on P & T)

P = (equilibrium) vapor pressure

T = temperature (K)

R = gas constant (8.314 J/K•mol)





The ***boiling point*** is the temperature at which the (equilibrium) vapor pressure of a liquid is equal to the external pressure.

The ***normal boiling point*** is the temperature at which a liquid boils when the external pressure is 1 atm.

TABLE 11.6 Molar Heats of Vaporization for Selected Liquids

Substance	Boiling Point* (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	80.1	31.0
Ethanol (C_2H_5OH)	78.3	39.3
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

* Measured at 1 atm.

The ***critical temperature*** (***T_c***) is the temperature above which the gas cannot be made to liquefy, no matter how great the applied pressure.

The ***critical pressure*** (***P_c***) is the minimum pressure that must be applied to bring about liquefaction at the critical temperature.

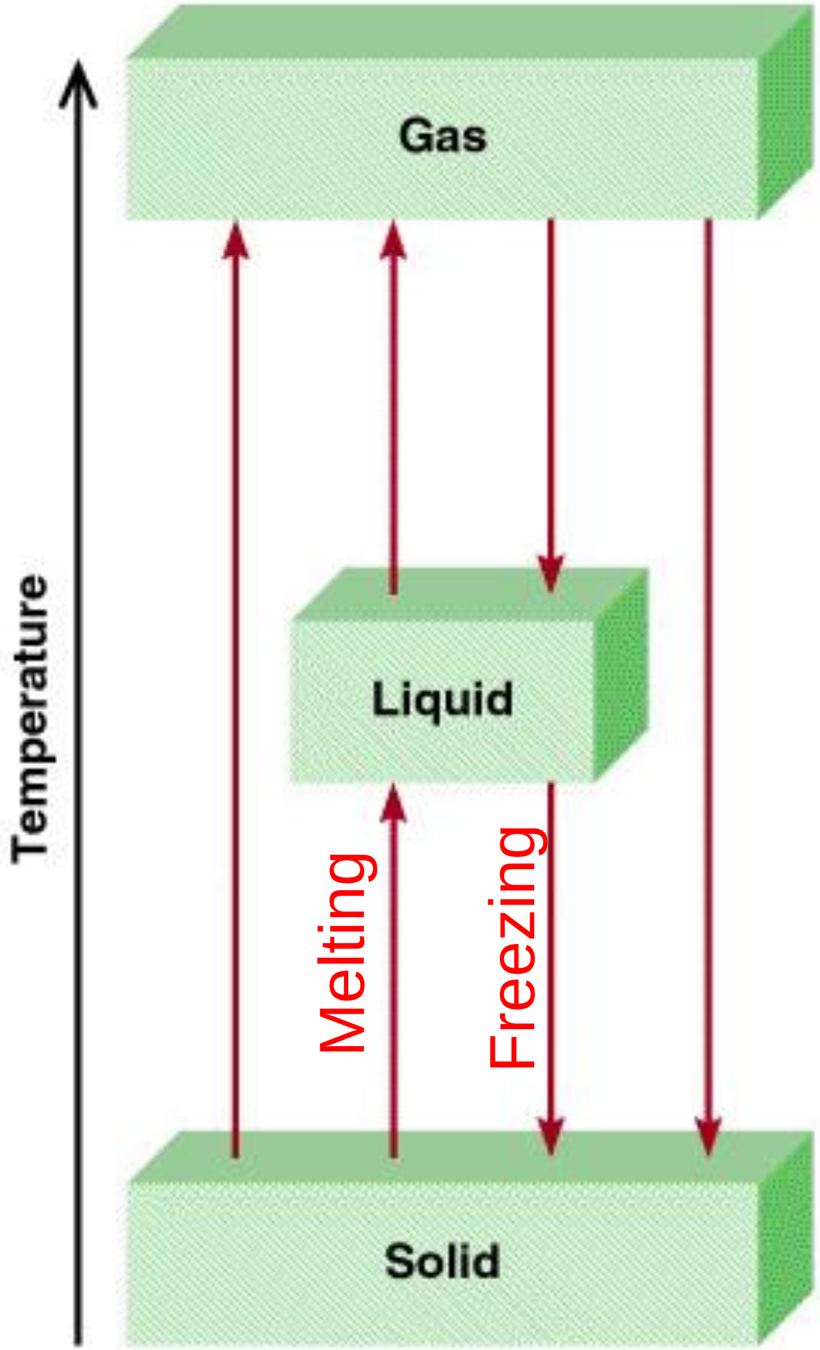
TABLE 11.7 Critical Temperatures and Critical Pressures of Selected Substances

Substance	T_c (°C)	P_c (atm)
Ammonia (NH_3)	132.4	111.5
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	288.9	47.9
Carbon dioxide (CO_2)	31.0	73.0
Ethanol (C_2H_5OH)	243	63.0
Diethyl ether ($C_2H_5OC_2H_5$)	192.6	35.6
Mercury (Hg)	1462	1036
Methane (CH_4)	−83.0	45.6
Molecular hydrogen (H_2)	−239.9	12.8
Molecular nitrogen (N_2)	−147.1	33.5
Molecular oxygen (O_2)	−118.8	49.7
Sulfur hexafluoride (SF_6)	45.5	37.6
Water (H_2O)	374.4	219.5

Phase Changes

$H_2O\ (s) \rightleftharpoons H_2O\ (l)$

The ***melting point*** of a solid or the ***freezing point*** of a liquid is the temperature at which the solid and liquid phases coexist in equilibrium



Molar heat of fusion (ΔH_{fus}) is the energy required to melt 1 mole of a solid substance.

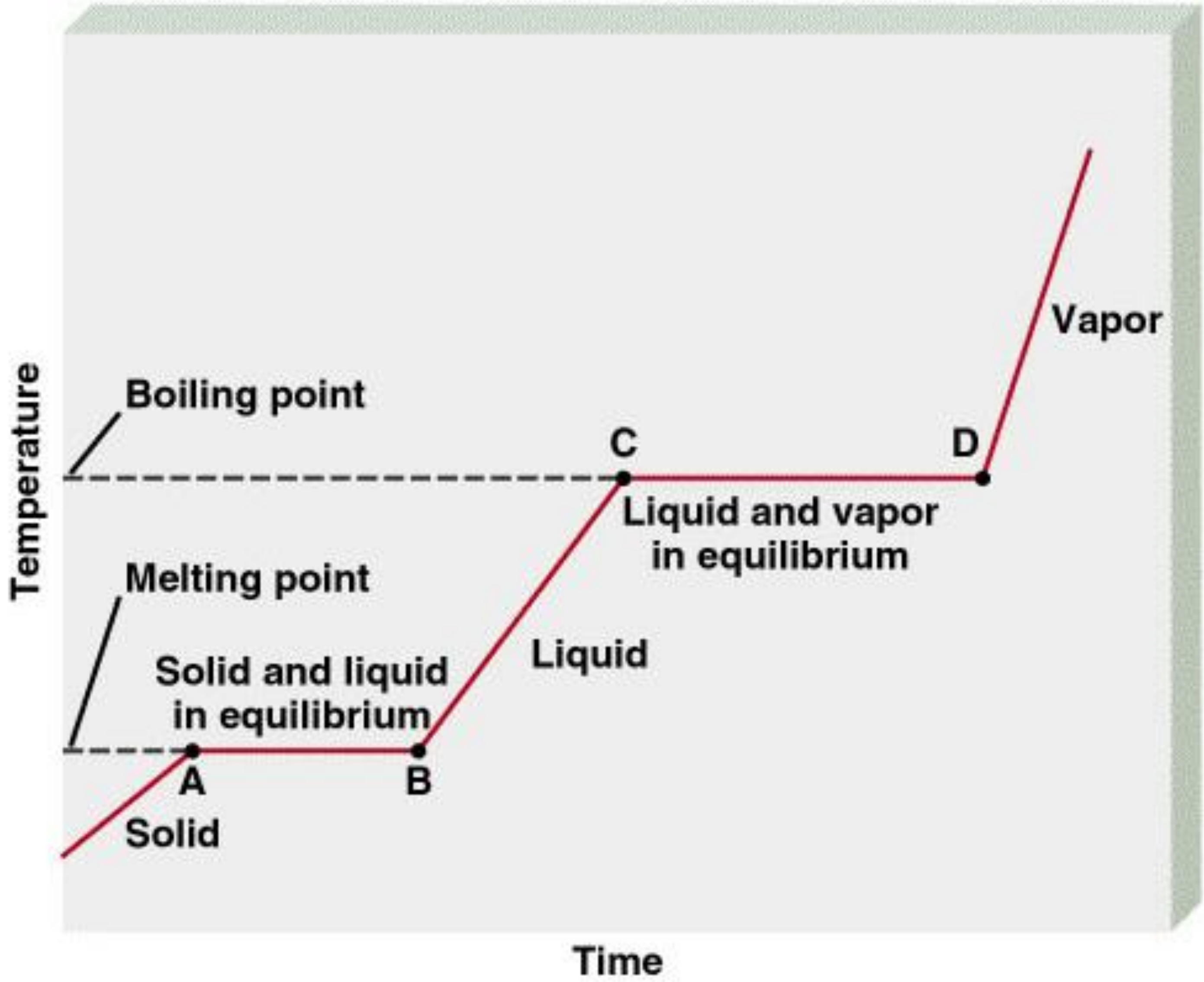
TABLE 11.8

Molar Heats of Fusion for Selected Substances

Substance	Melting Point* (°C)	ΔH_{fus} (kJ/mol)
Argon (Ar)	−190	1.3
Benzene (C_6H_6)	5.5	10.9
Ethanol (C_2H_5OH)	−117.3	7.61
Diethyl ether ($C_2H_5OC_2H_5$)	−116.2	6.90
Mercury (Hg)	−39	23.4
Methane (CH_4)	−183	0.84
Water (H_2O)	0	6.01

* Measured at 1 atm.

Heating Curve



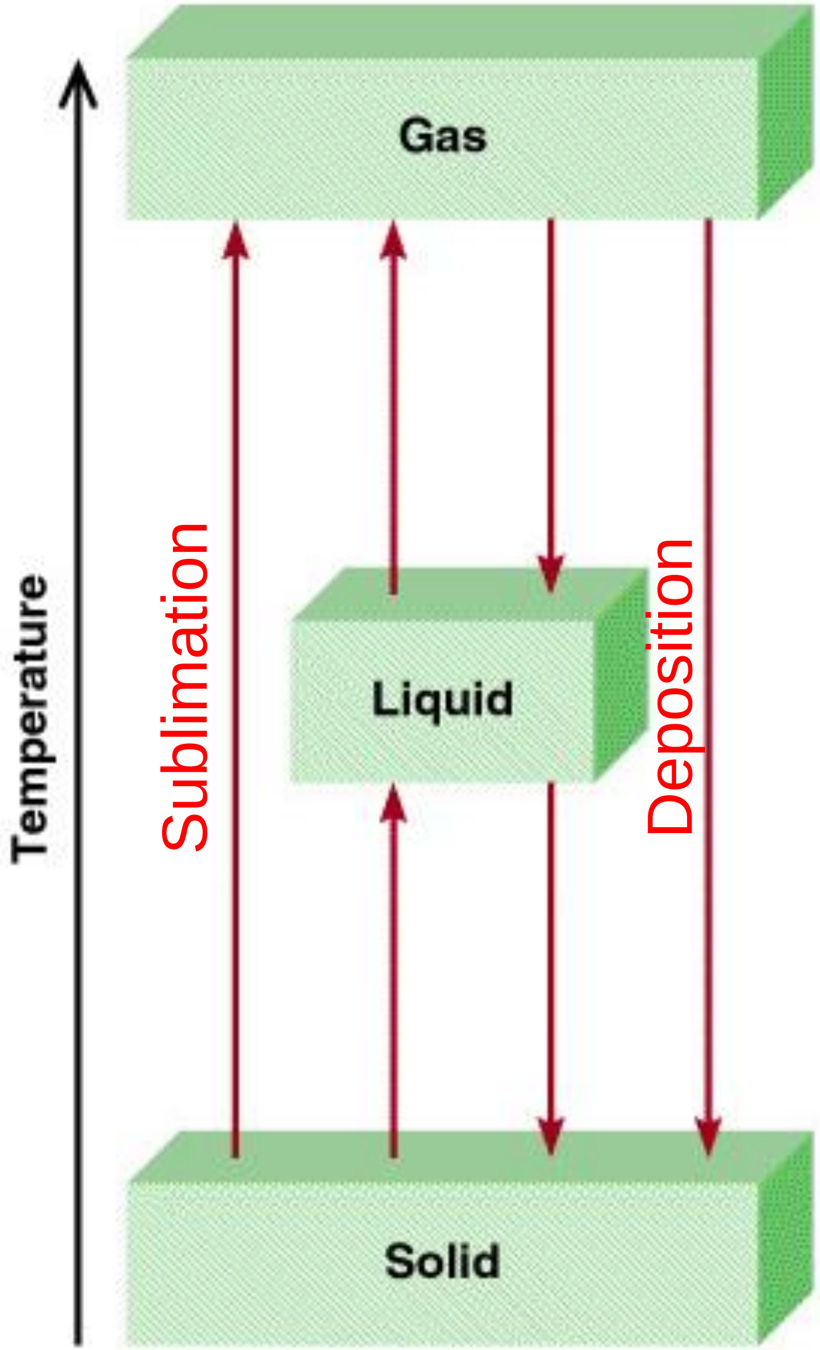
Phase Changes

$H_2O\ (s) \rightleftharpoons H_2O\ (g)$

Molar heat of sublimation (ΔH_{sub}) is the energy required to sublime 1 mole of a solid.

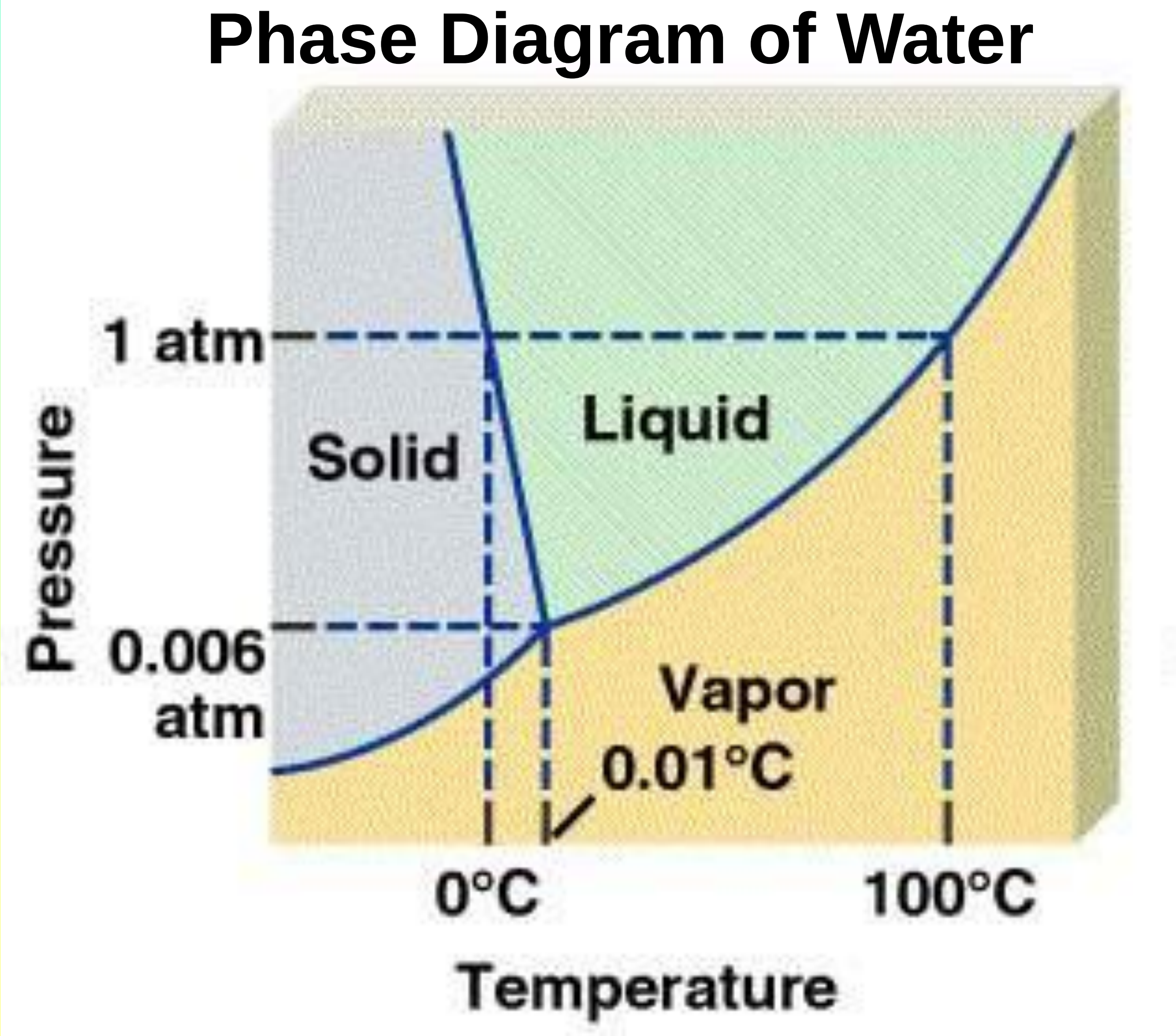
$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

(Hess's Law)

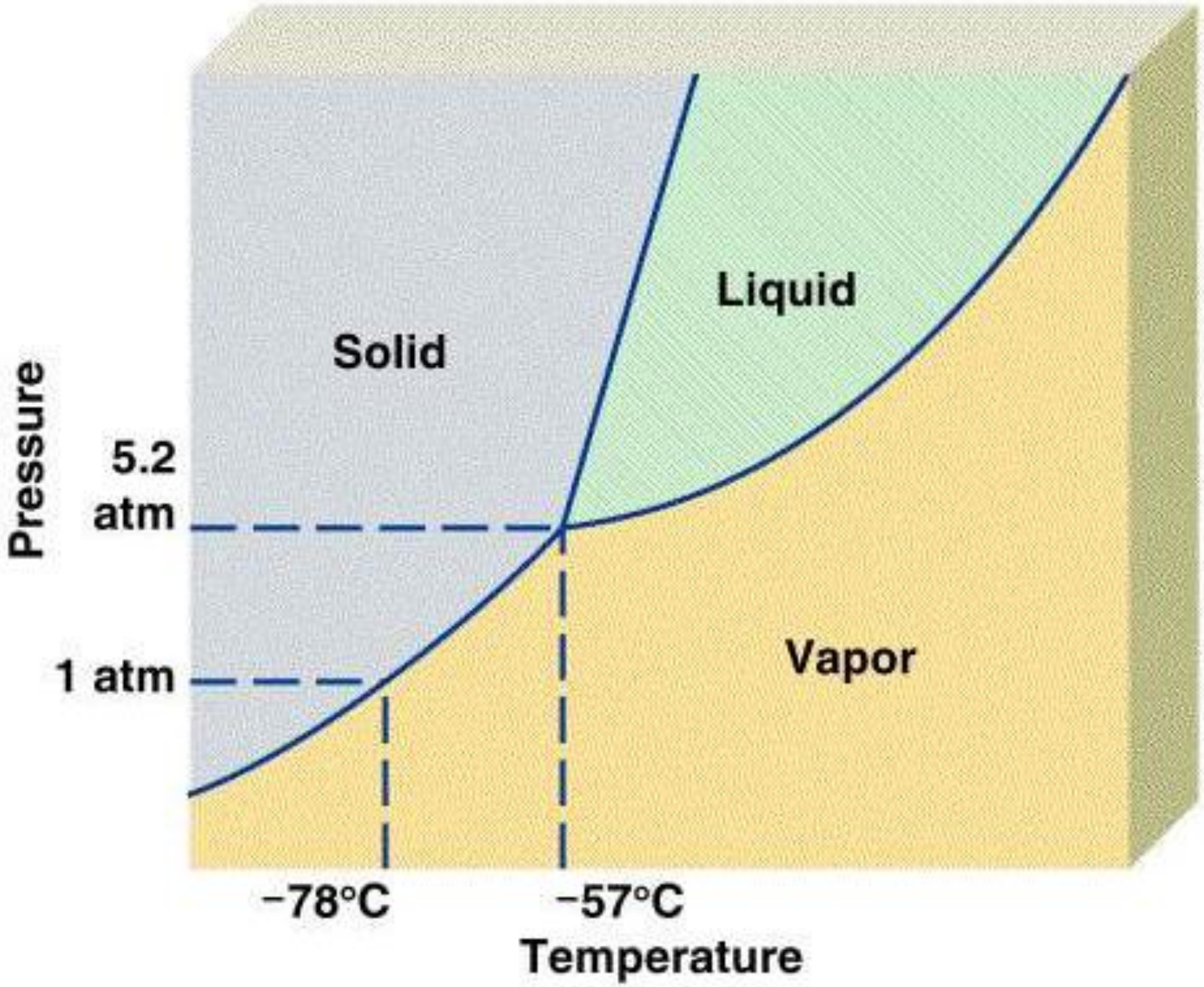


A ***phase diagram*** summarizes the conditions at which a substance exists as a solid, liquid, or gas.

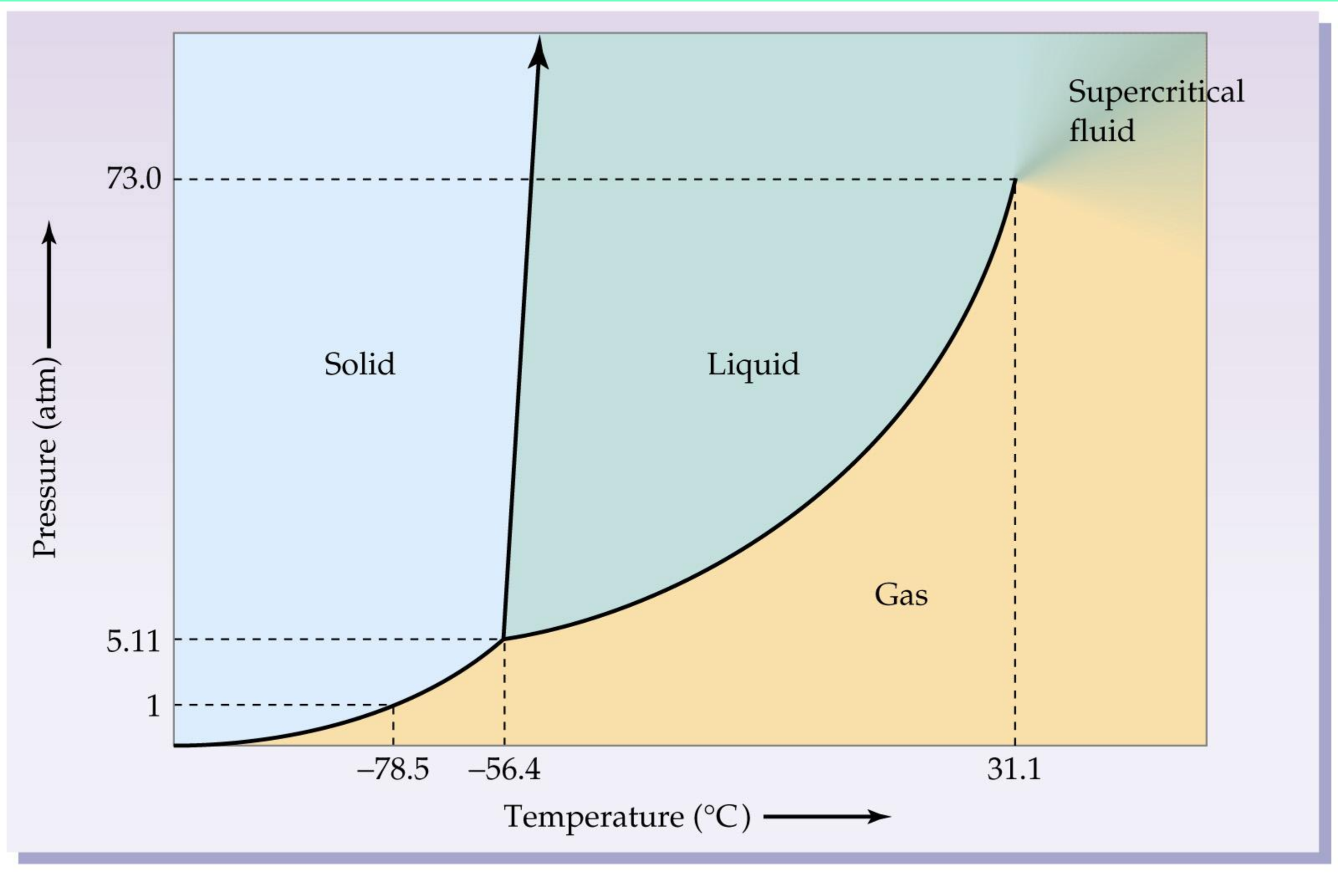
The ***triple point*** is where all 3 phases meet.



Phase Diagram of Carbon Dioxide



Where's Waldo?



Carbon Dioxide

Can you find…

The Triple Point?

Critical pressure?

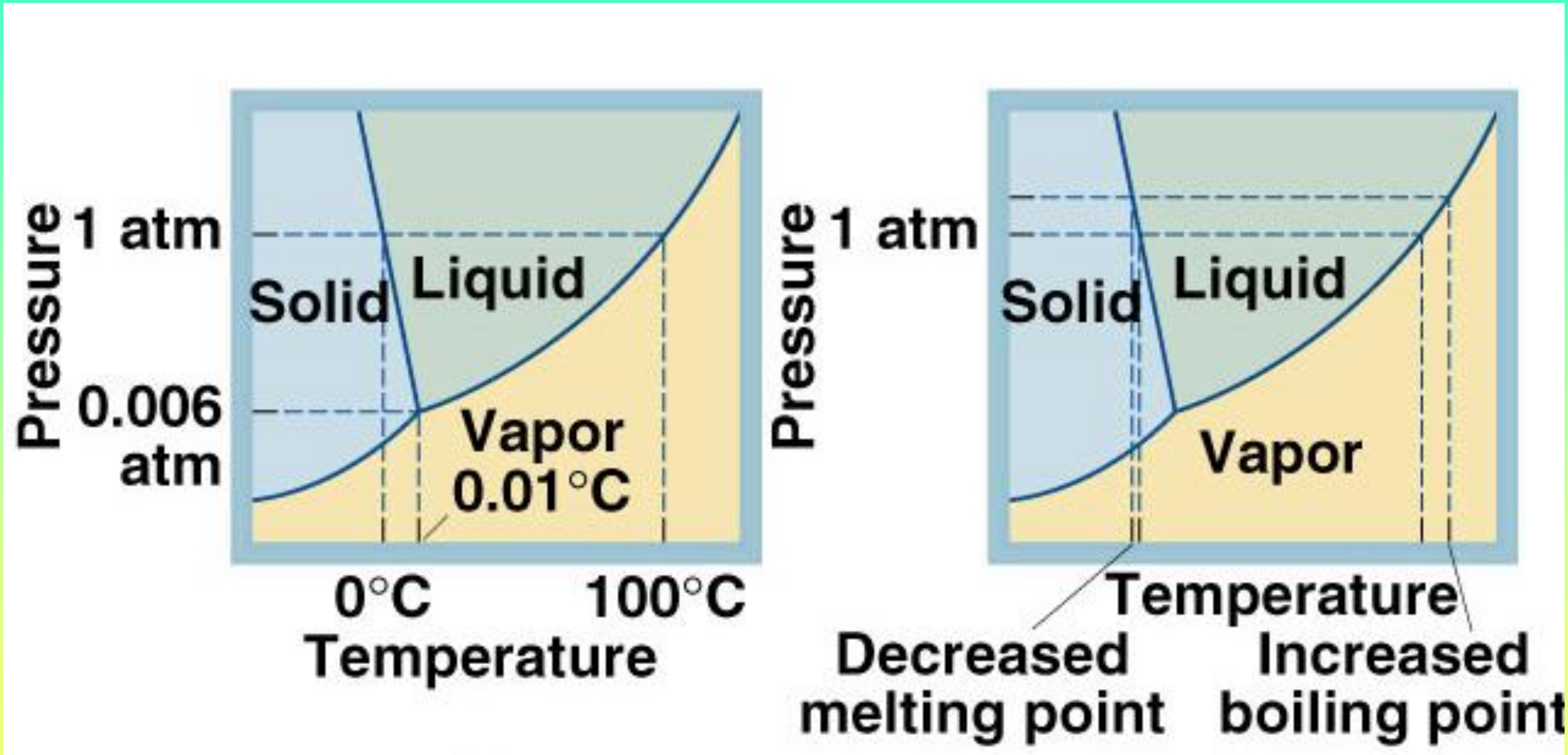
Critical temperature?

Where fusion occurs?

Where vaporization occurs?

Melting point (at 1 atm)?

Boiling point (at 6 atm)?


Pressure
1 atm
0.006
atm
Solid
Liquid
Vapor
0.01°C
0°C
100°C
Temperature
Pressure
1 atm
Solid
Liquid
Vapor
Temperature
Decreased
melting point
Increased
boiling point

Chemistry In Action: Liquid Crystals